



# Removal of natural organic matter for drinking water production by Al/Fe-PILC-catalyzed wet peroxide oxidation: Effect of the catalyst preparation from concentrated precursors

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## ABSTRACT

Catalytic wet peroxide oxidation (CWPO) has been assessed at semi-batch lab scale for the removal of natural organic matter (NOM) from raw surface water currently employed as feedstock in a drinking water treatment's plant. The peroxide solution has been stepwise added and its catalytic activation carried out by Al/Fe-pillared clays prepared from concentrated or diluted both, metal precursor solutions and clay suspensions (aqueous or ethanolic). An improved hydrolysis ratio ( $\text{OH}/(\text{Al} + \text{Fe})$ ) of 1.6 was found by Ferron analyses for the preparation of the concentrated metal precursor ( $[\text{Al} + \text{Fe}] = 0.628 \text{ mol/dm}^3$ ), without significant metal loss by precipitation. Increased concentration of the pillaring precursor solution led to: (i) slightly decreased and (ii) more broadly distributed XRD-basal spacings, but also (iii) higher cationic compensation on the starting clay. Ethanol as suspension medium enabled the oligomer intercalation to be less susceptible against the clay concentration. It was achieved up to 96% of chemical oxygen demand (COD) removal in 4 h and total color removal in less than 45 min of reaction for a selected catalyst, under very mild conditions of room temperature and atmospheric pressure. The clay catalysts displayed high chemical stability against iron leaching. In addition, the solid prepared from the concentrated metal precursor in a 25% (w/v) ethanolic suspension successfully performed in a high demanding catalytic test, which involved very high humic substrate-to-catalyst ratio, prolonged time of reaction (24 h) and close to neutral pH of reaction (7.5), identical to that featured by the raw surface water.

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## 1. Introduction

One of the environmental concerns lately more studied is the efficient and affordable recovery of water resources contaminated with toxic organic compounds. Although the vast majority of the studies dealing with wastewater treatment to remove organic matter have involved microbiological steps as the best cost/benefit approach [1], this kind of technological application for feedstock refinement must be avoided in the production of drinking water. Microbiological safety is of course mandatory for these effluents and this is why disinfection is one of the stages demanding more care in the production of drinking water.

Although the removal of natural organic matter (NOM) from water resources has been usually solved by applying conventional coagulation/flocculation processes [2], a considerable increase in the content of NOM in surface waters has been observed during the past 25 years [3], in some cases, very difficult to be removed by standard physicochemical techniques. NOM brings many problems in drinking water treatment processes, including: (i) negative effect on water quality by color, taste and odor problems, (ii) increased coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful formation of disinfection by-products (DBPs), (iii) promoted biological growth in distribution systems, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants [4]. Therefore, the application of advanced oxidation processes (AOPs) for the treatment of surface streams in the production of drinking water has recently attracted a great interest. The AOPs are a set of technologies addressed to afford a continuous generation of hydroxyl radicals ( $\text{HO}^\bullet$ ) by catalytic, photolytic, photo-catalytic, etc. strategies of activation, which are

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able to deplete a wide range of organic substances otherwise difficult to biodegrade [5].

Several studies have been recently devoted to find out the potential role that AOPs may play in the removal of NOM from natural waters. Most of them have assessed techniques where activation is carried out by means of radiation or dissolved catalysts [4], for instance: UV-light based applications (UV/H<sub>2</sub>O<sub>2</sub>) [6]; ozone based applications (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>) [7,8]; heterogeneous photo-catalysis (TiO<sub>2</sub>/UV) [9] and Fenton homogeneous processes [10]. Although activation by solid catalysts displays clear advantages in terms of active site reusability and easier separation from the final effluent, till now the ability of heterogeneous Fenton-like catalyzed processes for NOM removal, other than those employing also some kind of radiation, has been rather scarcely studied in this application.

Among the AOPs, strong efforts are being done to develop solid catalysts able to generate the reactive radicals under ambient conditions of temperature and pressure, often being referred to as catalytic wet peroxide oxidation (CWPO). The Al/Fe-pillared clays constitute one of the most promising groups of structured materials that have successfully accomplished such a task [11,12]. Pillaring of natural or synthetic clays consists in the intercalation of voluminous inorganic polycations driven by cationic exchange, wherein by far the system more studied has been the tri-decameric Keggin polycation (Al<sub>13</sub>)<sup>7+</sup> [13,14]. Thus, the structural sheets of the hosting aluminosilicate are stabilized upon thermal treatment in a swollen form, delivering a nanostructured wafer-shaped set of channels available for adsorption and catalysis. Since they can be usually prepared from natural clays quite abundant worldwide, the resulting modified materials display remarkable applicability to solve environmental problems at big scale, under low cost.

Therefore, several works have been recently devoted to optimize some variables for the preparation of Al/Fe-PILCs like the hydrolysis ratio (HR, the molar ratio hydroxyl/metals) [11] and the atomic metal ratio (AMR, the amount of a pillaring metal referred to the total amount of them in mixed pillaring solutions) [12]. However, the method of preparation still needs to be further improved in order to efficiently work on concentrated suspensions. Conventional procedures for preparation of pillared clays involve slow dropping of low concentrated metal oligomeric solutions (typical total metal concentration <0.1 mol/dm<sup>3</sup>) on diluted clay suspensions (commonly, 2–5%, w/v), consuming significant volumes of water [15]. Although some investigations have recently faced on this problem applying microwaves or ultrasound [16,17] along the step of clay intercalation in concentrated suspensions with promising results, it obviously implies the consumption of an extra amount of energy. Storaro et al. [18] proposed some time ago that by using a solvent with low dielectric constant like acetone rather than water as suspension medium, the intercalation of completely unrefined Ca-rich smectites was improved, avoiding its gelation along the process even in highly concentrated clay suspensions. It is worth noting that calcium-rich aluminosilicates are one of the most commonly occurring cationic forms of smectites in nature [19]. Moreover, to our best knowledge the use of cheaper, less volatile and more easily handled solvents also featuring low dielectric constant like ethanol, has not been assessed as suspension medium for this preparative approach.

Aiming to contribute in the same sense, some methodologies to generate Keggin-like aluminum oligomeric pillaring precursors under concentrated conditions have been tested. Among others, preparation from concentrated metal solutions [20,21] and generation of a solid polymeric precursor from sulfate precipitation followed by nitrate metathesis [22,23] can be mentioned. Moreover, it has been realized as a big trouble that either, final metal concentrations higher to 0.2 mol/dm<sup>3</sup> in the partially hydrolyzed solutions [20] and/or HR values lower than 1.5 [24] conduce to

meaningful decrease in the fraction of the metals forming Keggin-like Al<sub>13</sub> pillaring species. Besides, to avoid significant precipitation of the metal hydroxides, the use of high concentrated metal solutions obligates to carry out the hydrolysis step using smaller base amounts and in turn lower final HR values than the typical range found optimal, 2.0–2.5 [24].

Therefore, in the present work pillared clays from both diluted or concentrated ethanol or water/clay suspensions and diluted or concentrated mixed (Al/Fe) metal oligomeric pillaring precursors were prepared. The proper HR value for the preparation of the concentrated mixed metal precursor, while minimizing the metal loss by precipitation, was previously established by Ferron analyses. The resulting materials were examined in the CWPO treatment of raw surface water, recording chemical oxygen demand (COD) and true color depletion profiles. The input stream is currently employed as feedstock of the Pasto (Colombia) city's drinking water treatment plant and satisfies the demand of close to half a million people. The reaction was carried out under semi-batch lab scale at room temperature and atmospheric pressure.

## 2. Experimental

### 2.1. Materials

The starting material for the preparation of the clay catalysts was a natural bentonite from the Cauca Valley region-Colombia, already carefully characterized [12,16]. Before the pillaring procedure, the raw mineral was particle-size refined by sedimentation ( $\leq 2 \mu\text{m}$  fraction), yielding a material (BV) with cationic exchange capacity (CEC) of 89 meq/100 g (dry basis). The mixed metal oligomeric precursor for pillaring was prepared employing AlCl<sub>3</sub>·6H<sub>2</sub>O ( $\geq 99\%$ , from Sigma-Aldrich), FeCl<sub>3</sub>·6H<sub>2</sub>O ( $\geq 99.5\%$ , from Mallinckrodt) and NaOH ( $\geq 99.8\%$ , from Mallinckrodt), all used as received. The clay suspensions were prepared in distilled water or ethanol ( $\geq 99.5\%$ , ACS reagent, from Sigma-Aldrich).

### 2.2. Preparation of the Al/Fe-mixed hydrolyzed solutions

Two Al-Fe mixed pillaring precursors, a diluted and a concentrated one, were prepared with identical Fe charge (AMR = 2.0%; Al/Fe molar ratio = 49). For reference purpose, a sample of the starting clay was also pillared with single Al-hydrolyzed solution (sample BVAI-W2), prepared according to the conventional procedure, that is, from diluted both pillaring solution and aqueous clay suspension. The mixed diluted precursor was prepared from a slightly modified conventional method already reported [12]. A couple of 0.2 mol/dm<sup>3</sup> AlCl<sub>3</sub>·6H<sub>2</sub>O and 0.2 mol/dm<sup>3</sup> FeCl<sub>3</sub>·6H<sub>2</sub>O solutions were mixed to reach the desired AMR value. Afterwards, a 0.2 mol/dm<sup>3</sup> NaOH solution was slowly added throughout 8 h at 343 K under reflux in proper amount to get a final molar hydrolysis ratio (OH/(Al + Fe)) of 2.0. The obtained solution, having a final metal concentration [Al + Fe] = 0.068 mol/dm<sup>3</sup>, was then left to cool down till room temperature before being added on the clay suspension.

In the case of the concentrated Al/Fe intercalating precursor, a similar methodology was used, excepting the following features: the mixed aqueous solution of metal chlorides was 2.23 mol/dm<sup>3</sup> [Al + Fe], which was thereafter hydrolyzed by a 1.2 mol/dm<sup>3</sup> NaOH solution getting a final HR value of 1.6. The final metal concentration [Al + Fe] was 0.628 mol/dm<sup>3</sup>.

### 2.3. Preparation of the catalysts

The procedure to prepare the mixed pillared clays was adapted from various literature reports [15,18]. The previously prepared either, diluted or concentrated Al- or Al/Fe-hydrolyzed solution was

**Table 1**

Conditions of preparation, CEC compensation, basal spacing, and Al and Fe contents of the clay catalysts.

Sample	[M] <sup>a</sup> (mol/dm <sup>3</sup> )	[BV] <sup>b</sup> (w/v%)	Suspension medium	HR <sup>c</sup>	CC <sup>d</sup> (%)	<i>d</i> <sub>001</sub> <sup>e</sup> (nm)	<i>fwhm</i> <sup>f</sup> (° 2θ)	Solid content	
								Al (wt. %)	Fe (wt. %)
BV	NA	NA	NA	NA	0	1.45	1.55	11.26	7.75
BVAI-W2	0.068	2.0	Water	2.0	81	1.92	1.35	15.32	7.67
BVAIFe2-W2	0.068	2.0	Water	2.0	55	1.97	1.15	15.55	8.51
BVAIFe2C-W2	0.628	2.0	Water	1.6	69	1.78	1.25	15.68	8.03
BVAIFe2C-W25	0.628	25.0	Water	1.6	66	1.93	1.10	15.80	8.29
BVAIFe2C-EtOH2	0.628	2.0	EtOH	1.6	73	1.84	1.55	NM	NM
BVAIFe2C-EtOH25	0.628	25.0	EtOH	1.6	69	1.80	1.48	15.86	8.47

<sup>a</sup> [M] = total metal concentration in the hydrolyzed precursor. M = Al or (Al + Fe).<sup>b</sup> [BV] = concentration of the clay suspension.<sup>c</sup> Hydrolysis ratio (see the text).<sup>d</sup> CC = percentage of the cationic-exchange capacity in the starting material that was compensated by the intercalating solution (see the text for more details).<sup>e</sup> Obtained from oriented specimens.<sup>f</sup> Full width at half maximum of the *d*<sub>001</sub> peak; NA = not applicable for this sample; NM = not measured.

slowly dropped under stirring (~1.5 cm<sup>3</sup>/min) onto a 2.0 or 25.0%, w/v ethanolic or aqueous suspension of the starting clay, always in sufficient amounts to get a final loading of 20 meq<sub>metals</sub>/g<sub>clay</sub>. Afterwards, the resulting suspension or kind of sludge was aged along 12 h at room temperature, thoroughly dialyzed (dialysis tubing cellulose membrane, D9527 Sigma–Aldrich) in distilled water to remove the ion excess, dried at 333 K and heated under air at 773 K for 2 h to obtain the final catalyst. The samples are designated starting by the clay mineral (BV), the metals involved, its iron AMR percentage, and the letter “C” only accounting for the materials prepared from the concentrated metal precursor, followed by “W” or “EtOH” for water or ethanol as suspension medium respectively, finishing with the clay’s concentration percentage (Table 1). Since every solid catalyst was prepared twice, the average physicochemical features are displayed.

#### 2.4. Analytical methods

X-ray diffraction (XRD) patterns of the clay catalysts were recorded over oriented specimens in a Siemens D-500 diffractometer, working at 40 kV and 30 mA with a scanning speed of 2°/min, employing Cu Kα filtered radiation (λ = 1.5418 Å). The elemental analyses of the solid materials were carried out by atomic absorption spectroscopy (AAS) in a PerkinElmer 3110 spectrometer.

The CEC of the solids was determined by saturation with 1.0 mol/dm<sup>3</sup> ammonium acetate solution under reflux, followed by repeated washing with distilled water and centrifugation to eliminate the excess of ammonium ions. The amount of retained ammonium was established by micro-Kjeldahl analysis. The results are interpreted in terms of the CEC compensation (CC) reached on the starting clay by the pillaring procedure, expressed as follows for a given *x* sample:

$$CCx(\%) = \left( \frac{(CEC_0 - CECx)}{CEC_0} \right) \times 100$$

where CEC<sub>0</sub> is the cationic exchange capacity of the starting clay, BV in this case, and CEC<sub>x</sub> is the value obtained for the given modified material *x*.

The HR value and the concentration of the metals to be employed in the preparation of the concentrated pillaring precursor were determined by a set of screening experiments. The relative concentration of Keggin-like species as a function of both, the HR value (2.0–2.5) and the starting concentration of the metals (0.2–1.0 mol/dm<sup>3</sup>) was measured by kinetic resolution at 366 nm using the Ferron reagent (8-hydroxy-7-iodo-5-quinolinesulfonic acid >99.0%, Aldrich), following the methodology reported by Feng et al. [24]. For preparation of the Ferron colorimetric solution, sodium acetate and hydrochloric acid, both A.R. grade, were also

used, employing a method from Feng et al. [25]. It has been recently shown that under low iron contents ([Fe]/[Al] ≤ 0.05), like in the present work, interference of this metal on the observed speciation can be safely neglected [25] and then simplified colorimetric solution was used. The total concentration of the dissolved Al and Fe was recorded by AAS on the metal precursors previously micro-filtered to remove precipitated moieties (0.45 μm membranes). Fraction (Al–Fe)<sub>a</sub> was determined from measured absorbance at 1.0 min of reaction, and the (Al–Fe)<sub>b</sub> one at 2.0 h of reaction for every solution. The metal content not detected with the reagent, that is, the difference between the total and the complexed amounts together with that precipitated along the hydrolysis treatment comprised the last measured Ferron fraction (Al–Fe)<sub>c</sub> (see detailed explanation in a forthcoming paragraph).

In order to meet the local quality control regulations, COD and true color were the parameters adopted to follow the NOM content in the aqueous streams. Both parameters were measured according to validated standard methodologies from APHA-AWWA-WPCF [26]. COD was determined using the closed reflux colorimetric method 5220D properly adapted to operate at low concentrations by measuring at 444 nm. True color (color<sub>455</sub>) was recorded at 455 nm by spectrophotometric single wavelength method 2120C, using a 500 platinum-cobalt units (PCU) standard color solution, from Hach Company. All the spectrophotometric measurements were made in a PerkinElmer lambda 11 instrument. The entire analytical measurements were replicated and the corresponding average values reported.

#### 2.5. Catalytic experiments

A unique sample of raw surface water was taken from Pasto River in the intake of the Centenario plant, the drinking water facility of Pasto city at southwest Colombia, stored at 277 K and used to perform all the catalytic runs (COD = 40.14 mg O<sub>2</sub>/dm<sup>3</sup>; color<sub>455</sub> = 42 PCU; pH 7.15; Cl<sup>−</sup> = 2.7 mg/dm<sup>3</sup>; P-total = 3.7 mg/dm<sup>3</sup>; N-total = 7.9 mg/dm<sup>3</sup>). Continuous monitoring of these parameters by the treatment’s plant operator on the raw surface water along a year 2010 showed a high seasonal variability in COD content (15–40 mg O<sub>2</sub>/dm<sup>3</sup>) as well as in apparent color (115–295 PCU). The catalytic oxidations were carried out using 450 cm<sup>3</sup> of the starting sample in a 500 cm<sup>3</sup> glass semi-batch reactor operating at room temperature and atmospheric pressure (291 K, 72 kPa), with continuous magnetic stirring of the reaction mixture (200 rpm). The pH was continuously controlled at 3.7 by dropping 0.1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> or NaOH solutions, according to the optimum value reported for Al/Fe-PILCs in the CWPO reaction [27]. The solid catalyst was added into the reaction vessel in one of two loadings, 0.5 g/dm<sup>3</sup> or 5.0 g/dm<sup>3</sup>, and the mixture kept under stirring by 15 min.

Then, 24.0 cm<sup>3</sup> of fresh-prepared 0.047 mol/dm<sup>3</sup> hydrogen peroxide solution, equivalent to the stoichiometric amount for complete oxidation according to the theoretical ratio of 1.0 mg/dm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> needed by every 470.6 mg O<sub>2</sub>/dm<sup>3</sup> of COD [28], started to be fed into the reacting recipient under a flow rate of 6.0 cm<sup>3</sup>/h. The addition of the catalyst to the system was taken as zero time of reaction, although peroxide addition only started 15 min later. Air bubbling was maintained along all the experiment under a constant flow rate. Periodic sampling was made throughout 4 h of reaction for every experiment. Samples of 4.0 cm<sup>3</sup> were immediately micro-filtered after taken (Millipore 0.45 μm), a fraction of 1.5 cm<sup>3</sup> was used to determine true color<sub>455</sub> while the remaining 2.5 cm<sup>3</sup> were employed for COD analysis for each one. The error introduced in the measurements by filter's NOM adsorption was offset by applying identical procedure on the starting stream (zero time of reaction) and by plotting COD and color depletion in percentage instead than absolute concentrations; 0.45 μm micro-filtering also avoided that settlement of suspended particles would partially explain observed NOM removal. The output streams were analyzed by AAS in a PerkinElmer 2380 atomic absorption spectrometer to determine Fe concentration, checking by this way the metal stability in the solid catalysts.

In order to estimate the catalyst reusability in terms of catalytic activity and chemical stability, a set of six semi-batch runs was performed using the same chosen best catalyst. For such a purpose, once finished every catalytic experiment the catalyst was separated by filtration, washed twice with distilled water on the same filter paper and finally dried at 333 K. In order to ensure comparability throughout all the series of reuses, the volumes of the influent water and the peroxide solution were properly adjusted every time to take into account the cumulative catalyst drained by sampling. In addition, a modified catalytic run was also carried out using the same material in prolonged operation under high demanding conditions of reaction. The procedure for such a catalytic experiment was identical to the already explained, excepting the following aspects. A sample of distilled water doped with completely soluble sodium humates stabilized at pH 7.5 (COD = 1185 mg O<sub>2</sub>/dm<sup>3</sup>; color<sub>455</sub> = 1100 PCU), was employed as highly concentrated substrate. The catalyst loading was set in 5.0 g/dm<sup>3</sup>, the concentration of the peroxide solution was 0.67 mol/dm<sup>3</sup>, its total volume 48 cm<sup>3</sup> and it was added to the reacting vessel at a flow rate of 2.0 cm<sup>3</sup>/h until a final reaction time of 24 h was reached. The pH of reaction was controlled all the time in 7.5, pretty close to the pH exhibited by the natural surface water of Pasto River. The fraction of soluble humic substances was previously extracted from a local leonardite with 1.0 mol/dm<sup>3</sup> NaOH solution, keeping constant the pH of the mixture at 7.5 to ensure full solubility under the conditions of the catalytic reaction. The leonardite is a surface lignite-type mineral characterized by a high content of humic substances, mainly humic acids [29]. It must be stressed that humic substances comprise a complex mixture of high molecular mass organic compounds that may resemble very closely the NOM usually polluting surface waters.

### 3. Results and discussion

#### 3.1. Characterization of the clay catalysts

First of all, it must be pointed out that a detailed study about the physicochemical properties displayed by this kind of mixed pillared clays is available in a preceding work [12]. Particularly relevant to the present study is the fact that Fe AMR values below 5.0% in the mixed system Al/Fe allowed the almost quantitative Fe uptake by the clay mineral respect to the planned one and the textural properties were not significantly affected with respect to the

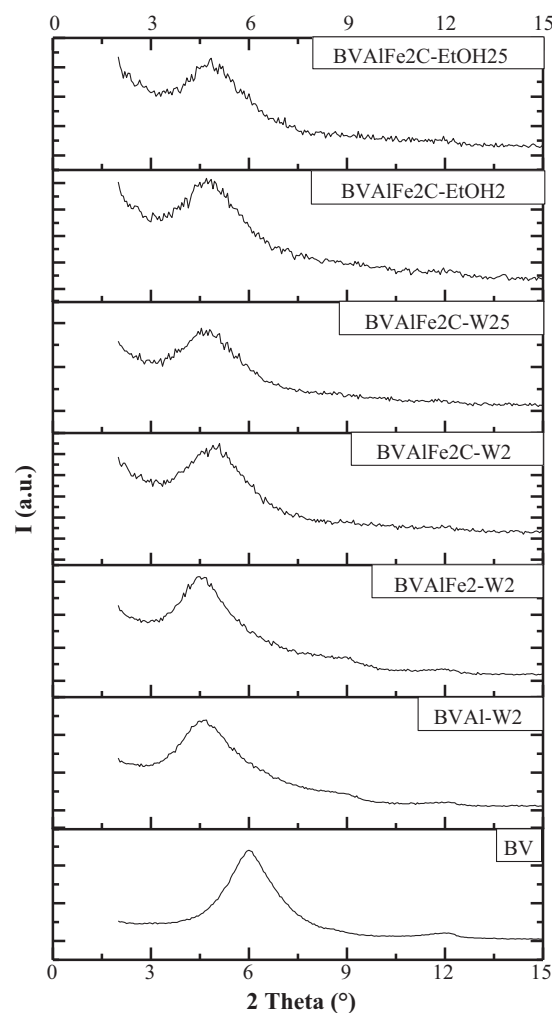


Fig. 1. Low angle region X-ray diffraction patterns of oriented specimens of the starting and the modified clay materials.

solid interlayered with single Al pillars (BVAIFe2-W2:  $S_{\text{BET}} = 155 \text{ m}^2/\text{g}$ ,  $S_{\text{EXT}} = 77 \text{ m}^2/\text{g}$ ,  $V_{\mu\text{p}} = 0.038 \text{ cm}^3/\text{g}$ ,  $V_{\text{ptotal}} = 0.120 \text{ cm}^3/\text{g}$ ). A strong correlation between the compensation of the cationic capacity (CC) and the catalytic performance of the resulting materials in the CWPO reaction was also evidenced. Besides, the stabilization of isolated species of the metal resulted clearly enhanced under the considered conditions of preparation, and the formation of aggregates of the metal oxide strongly minimized. It must be stressed that isolated species of iron are believed to be the main responsible for the improved catalytic activity of Al/Fe-PILCs in the CWPO reaction [12,27,30], while the extra-structural oxide aggregates appeared responsible for the leaching of the active metal under the oxidizing environment of reaction.

The expansion of the starting clay upon the pillaring processes was monitored by X-ray diffraction of oriented specimens. The low-angle patterns of the starting material (BV) and the clay after being modified under different conditions are compared in Fig. 1. It can be seen that expansions of the starting material from around 1.45 nm (peak centered at 6.0°) were obtained in all the cases up to basal spacing values ( $d_{001}$ ) between 1.78 and 1.97 nm. It is also noteworthy that higher concentration of metals in the mixed pillaring precursor led to broader basal spacing distribution (compare *fwhm* values for BVAIFe<sub>2</sub>-W2 and BVAIFe<sub>2</sub>C-W2 in Table 1). However, since the material pillared with single Al polycations (BVAIFe2-W2), irrespective the concentration of the pillaring precursor, exhibited a broader peak distribution (*fwhm* = 1.35° 2θ) than



**Table 2**

Ferron speciation of mixed metal pillaring precursors as a function of the total metal concentration and the hydrolysis ratio.

Sample	TMC <sup>a</sup> (mol/dm <sup>3</sup> )	HR <sup>b</sup>	(Al–Fe) <sub>a</sub> <sup>c</sup>	(Al–Fe) <sub>b</sub> <sup>d</sup>	(Al–Fe) <sub>c</sub> <sup>e</sup>	Al <sub>dis.</sub> <sup>f</sup> (%)	Fe <sub>dis.</sub> <sup>g</sup> (%)
TMC <sub>0.2</sub> HR <sub>2.00</sub>	0.2	2.00	0.179	0.302	0.519	99.9	96.7
TMC <sub>0.2</sub> HR <sub>2.25</sub>	0.2	2.25	0.134	0.285	0.581	99.3	98.5
TMC <sub>0.2</sub> HR <sub>2.50</sub>	0.2	2.50	0.159	0.335	0.506	96.5	87.6
TMC <sub>0.6</sub> HR <sub>2.00</sub>	0.6	2.00	0.220	0.140	0.640	98.8	86.3
TMC <sub>0.6</sub> HR <sub>2.25</sub>	0.6	2.25	0.163	0.130	0.707	97.4	79.5
TMC <sub>0.6</sub> HR <sub>2.50</sub>	0.6	2.50	0.215	0.127	0.657	99.4	96.4
TMC <sub>1.0</sub> HR <sub>2.00</sub>	1.0	2.00	0.226	0.141	0.633	85.6	82.1
TMC <sub>1.0</sub> HR <sub>2.25</sub>	1.0	2.25	0.124	0.130	0.746	88.8	75.7
TMC <sub>1.0</sub> HR <sub>2.50</sub>	1.0	2.50	0.057	0.115	0.828	62.7	58.8
Concentrated precursor	0.628	1.60	0.605	0.215	0.179	99.4	99.2

<sup>a</sup> TMC = total metal concentration in the final hydrolyzed precursor.<sup>b</sup> HR = hydrolysis ratio (see the text).<sup>c</sup> (Al–Fe)<sub>a</sub> = Ferron Al and Fe monomers, dimers and low oligomers.<sup>d</sup> (Al–Fe)<sub>b</sub> = Ferron Al and Fe Keggin-like oligomers.<sup>e</sup> (Al–Fe)<sub>c</sub> = Non Ferron detectable and precipitated Al and Fe high polymers and colloidal species.<sup>f</sup> Al<sub>dis.</sub> = aluminum dissolved in final metal precursor.<sup>g</sup> Fe<sub>dis.</sub> = iron dissolved in final metal precursor.

both Al/Fe-modified solids obtained from aqueous diluted clay suspensions, it can be inferred that the presence of Fe at low AMR apparently improved the distribution of the Al-based oligomers into the clay's interlayer space. There is also a slight increase in the attained top basal spacing using diluted both metal precursor and clay suspension when the second metal is involved in the pillaring precursor. Moreover, it is accompanied by a significant decrease in the cationic compensation (CC) accomplished by the mixed pillaring oligomers. Considering that the presence of iron gives a more acidic environment to the hydrolysis solution, the formation of highly condensed oligocations based in Al is probably more prevented, leading to narrower size and charge polycation distribution.

Regarding the HR value adopted in the preparation of the concentrated metal precursor, although as aforesaid several studies have evidenced that better intercalation of clays with Al/Fe mixed oligomeric solutions in diluted systems takes place in the range of HR 2.0–2.5 [11,15], the final pH of the solution once finished the hydrolysis step and then also the metal speciation might result strongly affected when starting from highly concentrated metal precursors [20]. Thus, a series of screening experiments (see Table 2) was performed in order to realize the combined effect of the total final metal concentration (TMC, in the range of 0.2–1.0 mol/dm<sup>3</sup>) and the HR value (2.0–2.5), on the fraction of the metals truly constituting Keggin-like intercalating species ((Al–Fe)<sub>b</sub>), by Ferron analyses. The Ferron reagent forms a chromophore complex with the aluminum species in liquid phase that can be easily recorded at 366 nm, whose generation takes place at different rates as a function of the degree of polymerization undergone by the metal. Thereby, the Ferron assay has been lately applied to distinguish three fractions: mononuclear Al, Al<sub>2</sub> and possibly Al<sub>6</sub> oligomers (Al<sub>a</sub>); reactive polymers mainly composed by Al<sub>13</sub> species and part of Al<sub>6</sub> oligomers (Al<sub>b</sub>) and inert high polymers or colloidal Al species (Al<sub>c</sub>), in hydroxyl-Al solutions [24,25]. In a similar way, considering the low proportion of Fe employed in the preparation of the metal precursors used in this work, the Ferron measurements are recorded in Table 2 in terms of the mixed metal fractions (Al–Fe)<sub>a</sub>, (Al–Fe)<sub>b</sub> and (Al–Fe)<sub>c</sub>, respectively.

The screening experiments showed that at low HR values the (Al–Fe)<sub>b</sub> fraction resulted clearly favored, although such effect became less pronounced at low TMCs. Besides, as can be seen, higher concentrations of the metals led to meaningful reduction in the (Al–Fe)<sub>b</sub> fraction for every HR, lowered final pHs together with increased fractions of the metals forming inert polymers colloids and sols, (Al–Fe)<sub>c</sub>. Finally, lower percentages of Al and Fe remained dissolved as the HR was increased for every TMC, this effect being

stronger for the higher metal concentration. It is ascribed to precipitation of single or mixed oxy-hydroxides of the metals throughout the hydrolysis stage, giving rise to variable loss of the metals in non-intercalating species.

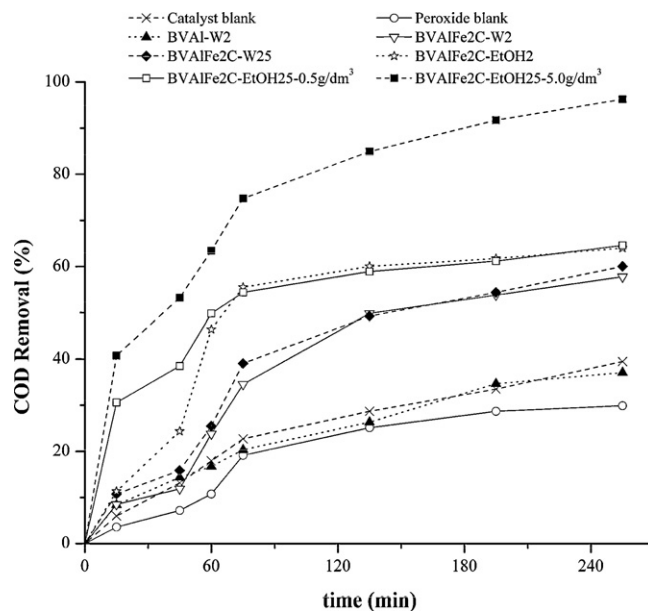
Then, further experiments were carried out on TMC 0.6 mol/dm<sup>3</sup>, in order to find out the low HR limit value for which the fraction of the metals lost by precipitation along the hydrolyzing step approached to zero (Al<sub>dis.</sub> and Fe<sub>dis.</sub> in Table 2 also approaching to 100%), while a significant (Al–Fe)<sub>b</sub> pillaring fraction remained in solution. Besides, the selected HR value still should exceed 1.5 as the limit below which aluminum condensation to Keggin-like polycations was reported to be seriously disfavored [24]. Such an improved HR was found to be 1.6 and for that reason this value was employed to prepare the concentrated mixed metal precursor used in the intercalation of the clay mineral. Furthermore, it was verified that relative (Al–Fe)<sub>b</sub> fraction in the finally selected concentrated precursor (TMC = 0.628 mol/dm<sup>3</sup>) remained even higher for HR = 1.6 (0.215) than for sample TMC<sub>0.6</sub>HR<sub>2.0</sub> (0.140). In addition, it was verified that metal loss under these conditions of preparation was insignificant (Table 2). Moreover, it must be pointed out that such a pillaring fraction anyway stayed smaller than the obtained for TMC<sub>0.2</sub>HR<sub>2.5</sub> (0.335), the biggest measured value among the samples prepared in the screening experiments. As said, it can be attributed to increased formation of “inert” (Al–Fe)<sub>c</sub> fraction accompanying the depletion in the values of the (Al–Fe)<sub>b</sub> fraction. However, the high (Al–Fe)<sub>a</sub> value displayed by the concentrated precursor also suggests that an important amount of low condensed products still remained in solution, probably due to the relatively low HR adopted.

The effect exerted by the concentration of the metal oligomeric precursor on the physico-chemical features of the obtained clay catalysts can be noticed by comparison of samples BVAIFe2-W2 and BVAIFe2C-W2 (Table 1 and Fig. 1). Higher concentration of the metals in the intercalating precursor led to lower basal spacing and less homogeneous oligomer distribution in the final material, but also higher cationic compensation was achieved on the starting clay. Besides, a lower amount of Fe was stabilized employing the concentrated precursor. It probably obeys to a broader size and charge distributions of the polycations formed upon the hydrolysis step, because of the different degrees of polymerization reached. In this sense, according to Chen et al. [20] the ε-Al<sub>13</sub> oligomers, [AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup>, may be significantly transformed to non Ferron-detectable (Al<sub>c</sub>), highly charged Al<sub>30</sub> polycations, [Al<sub>30</sub>O<sub>8</sub>(OH)<sub>56</sub>(H<sub>2</sub>O)<sub>24</sub>]<sup>18+</sup>, together with increased clustering to sol-like polymers, under high metal concentration and prolonged thermal treatment (*T* ~ 353 K; *t* ≥ 6 h of reaction),

conditions close to those used in the present work. This could explain the simultaneous higher *fwhm* and CC values displayed by the material pillared with the concentrated metal precursor against that treated with the diluted one. Although  $\text{Al}_{30}$  species could be expected *a priori* to develop larger basal spacings than  $\text{Al}_{13}$  when intercalated in cationic clays, literature reports about the preparation of  $\text{Al}_{30}$ -PILCs are not still available. Furthermore, it must be here stressed that the structure of  $\text{Al}_{30}$  polycations can be depicted as a couple of  $\text{Al}_{13}$  units linked by a tetra-nuclear crown of the metal [31,32], by which the interlayer expansion of the clay mineral would be not necessarily larger than the statistical diameter of the  $\text{Al}_{13}$  polycation ( $\sim 0.88$  nm). Thereafter, it can be inferred that the low Ferron ( $\text{Al-Fe}$ )<sub>b</sub> fraction measured in the concentrated mixed precursor cannot be straightforwardly interpreted as a decreased intercalating power of the oligomeric species generated therein. That is, the entire ( $\text{Al-Fe}$ )<sub>c</sub> fraction measured by the Ferron analysis on hydrolyzed aluminum-based precursors could not be considered so inert for pillaring purposes, when the preparation involves a prolonged time of thermal treatment under a relatively high temperature. In fact, the fairly enhanced cationic charge displayed by  $\text{Al}_{30}$  units would compensate de CEC of the starting clay in higher extent than Keggin-like polycations alone, probably explaining the enhanced CC of the materials prepared from the concentrated precursor.

The effect of the concentration of clay aqueous suspensions on the intercalating profile can be discussed from samples BVAIFe2C-W2 and BVAIFe2C-W25. It is remarkable that as the concentration of the clay suspension was increased more than twelve times (Table 1), both basal spacing and oligomer distribution resulted clearly enhanced, whereas the cationic compensation, Fe and Al uptakes remained all almost unaffected. This effect could be ascribed to the decreased pH of the aqueous clay suspension as the clay concentration rose ( $\text{pH}_{(2\%, \text{w/v})} = 5.13$ ;  $\text{pH}_{(25\%, \text{w/v})} = 4.77$ ). Considering that the pH of the concentrated pillaring precursor was 3.81, it is expectable that as the clay suspension exceeds this value it may greatly affect the size and charge distribution of the pillaring species. It is noteworthy that the equilibrium of the metal species present in Al/Fe oligomeric precursors is fairly more likely to be destabilized by pH effects under concentrated conditions, leading to greater fraction of highly condensed polymer species to be formed, which are more difficult to be exchanged. It may arise not only to the increased metal concentration but also to the presence of iron into the oligomer's framework, or even as a monomer, which may readily develop hydroxide particles even under rather acidic environments. Note in Table 2 that ( $\text{Fe}_{\text{dis}}$ ) was more seriously affected against HR than ( $\text{Al}_{\text{dis}}$ ) once higher metal concentrations were used. As the more concentrated aqueous clay suspension provided more acidic conditions itself, it seems that the intercalating step was apparently conducted under more favorable conditions, by allowing lower polycation decomposition than in the diluted one. It resulted not only in a narrower oligomer size distribution, but also in enhanced expansion of the clay layers and slightly increased amounts of aluminum and iron incorporated in the final material.

This behavior was not fully reproduced for the samples prepared using ethanol as a suspension medium (BVAIFe2C-EtOH2; BVAIFe2C-EtOH25). In spite of the slightly lower *fwhm* value obtained in the more concentrated clay suspension, the basal spacing remained almost unaffected with respect to the diluted one. This behavior may be due to the lower polarity provided by the organic solvent, preventing the aforementioned pH effect to play the foremost role, but may be also due to swelling restrictions imposed by using ethanol to suspend the montmorillonite. The oxophilic alkaline-earth Ca cations are known for maximizing the energy of the cation–dipole interactions with small polar compounds like ethanol and acetone [33]. Hence, ethanol may



**Fig. 2.** COD removals from raw surface water displayed by the clay catalysts. Set up:  $[\text{COD}]_0 = 40.14 \text{ mgO}_2/\text{dm}^3$ ; catalyst loading =  $0.5 \text{ g}/\text{dm}^3$  for all solids excepting sample BVAIFe2C-EtOH25-5.0  $\text{g}/\text{dm}^3$ ;  $[\text{H}_2\text{O}_2]_{\text{added}} = 0.047 \text{ mol}/\text{dm}^3$ ;  $\text{H}_2\text{O}_2$  addition flow rate =  $6.0 \text{ cm}^3/\text{h}$ ; final stoichiometric ratio  $[\text{H}_2\text{O}_2]/[\text{COD}]_0 = 1.0$ ; pH of reaction = 3.7; temperature =  $291 \pm 2.0 \text{ K}$ ; pressure =  $72 \text{ kPa}$ .

form interlayered complexes with the cation, but leading to basal spacings never exceeding  $1.9 \text{ nm}$  [18]. In addition, the decreased dielectric constant displayed by ethanol ( $24.3$ ) comparable to that of acetone ( $19.1$ ) [34], should enable the disposition of the calcium-rich clay particles to favor face-to-face aggregates more than in water ( $80.1$ ), but avoiding gelation or excessive dispersion that would take place with the sodium-rich form of the aluminosilicate or inefficient intercalation of the pillaring precursor to occur. Sodium-rich bentonites are well known for swelling almost indefinitely [35], while their calcium-rich counterparts have been reported to be strongly reluctant to gelation in aqueous or acetone-based suspensions up to rather high concentrations ( $50\%$ , w/v) [18]. Therefore, given the strong calcium character of the starting clay, apparently the gelation phenomenon did not affect in great extent the intercalation step even in the aqueous system for the range of clay concentrations here studied. In addition, it is also verified that change of the suspension medium from water to ethanol in the concentrated level (BVAIFe2C-W25 and BVAIFe2C-EtOH25) led almost to the same final contents of Al and Fe in the clay catalysts. Finally, the basal spacings displayed by the clay materials modified in ethanol suspension were close to  $1.8 \text{ nm}$  either, under low or high concentration, probably because of the swelling restrictions imposed by the use of the organic solvent.

### 3.2. Catalytic performance of the clay catalysts

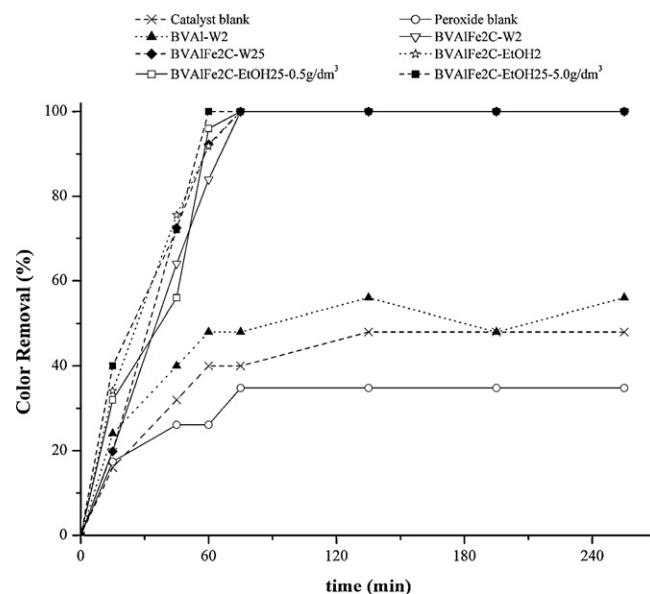
The catalytic performance of the materials in terms of COD removal is compared in Fig. 2 against a catalyst blank (catalyst BVAIFe2-W2 with no peroxide added) and a peroxide blank (only peroxide with no catalyst added). In order to better point out the roles played by the iron incorporated on the clay catalysts through the pillaring process and the textural effects, the catalytic profile of sample BVAIFe2-W2 is also included. It is shown that in spite of the low Fe AMR employed in the preparation of the pillaring precursors ( $2.0\%$ ) and the low amounts of Fe introduced in final materials (less than  $1.0 \text{ wt.}\%$ ; see Table 1), this quantity has a significant impact on the catalytic performance of the resulting materials. Moreover, it is also ruled out that simple adsorption might explain the differences

in the COD removal displayed by Fe-clay catalysts, considering that specific surface and polar affinity of solid BVAI-W2 are quite comparable with respect to the properties of the Al/Fe mixed pillared clay prepared under the same conditions (BVAIFe2-W2, curve “catalyst blank” in Fig. 2). In addition, the pretty low COD removal exhibited by the solid BVAI-W2 also shows that the iron content of the starting clay is not responsible for the high catalytic activity displayed by the pillared clays. The comparison with the “peroxide blank” reveals the very important role played by the catalysts in the activation of the oxidizing agent, leading to highly reactive hydroxyl radicals; the COD removal raised not over 30% after 4 h of reaction in presence of the stoichiometric amount of peroxide and catalyst absence. Once the iron-modified clays were also added, the value raised to 64.6% for a catalyst loading of  $0.5 \text{ g/dm}^3$ , or up to almost complete NOM depletion (96.3% COD removal) at the same time of reaction, as can be seen for  $5.0 \text{ g/dm}^3$  of catalyst BVAIFe2C-EtOH25.

Replacement of water by ethanol as suspension medium in the pillaring process not only did not decrease but even enhanced the catalytic performance of the catalysts prepared from the concentrated metal precursor (lets compare catalytic behavior of samples BVAIFe2C-W2 and BVAIFe2C-EtOH2). This enhancing was reflected both in the top COD removal reached at 4 h of reaction and, still more remarkable, in the faster contaminant depletion achieved at low times of reaction. At 75 min, corresponding to 60 min of oxidizing reaction, the COD removal of BVAIFe2C-W2 rose until close to 35% while BVAIFe2C-EtOH2 attained 55%. For the same series of solids but modified in clay suspensions of 25%, w/v, analogous behavior was verified probably also explained by slightly higher incorporation of iron (8.47% versus 8.29 wt.%), though showing slightly less different COD removals (39% and 54%, respectively). It indicates that in spite of the lower and broadly distributed basal spacings exhibited by the materials modified in EtOH-suspensions (see Table 1), the intercalation and stabilization of the metal oligomers leading to true mixed pillars was apparently better performed in the presence of the organic solvent. Besides, this pair of solids also featured slightly higher cationic compensation (CC) than their respective water-based suspensions.

On the other hand, when a ten-fold higher loading of the catalyst prepared under concentrated conditions in EtOH was applied (run BVAIFe2C-EtOH25- $5.0 \text{ g/dm}^3$ ), a further improvement of the catalytic performance can be seen in terms of both the top COD removal achieved and the lower time of contaminant depletion. This must be due to the presence of higher amount of metal sites available to catalyze the peroxide activation, while of course higher contribution of contaminant adsorption during the first 15 min of reaction is also evidenced. Finally, it must be stressed the presence of a kind of induction period taking place right after the equilibration step, in turn occurring along the first plotted 15 min without peroxide addition. It could be due to competition between peroxide and NOM molecules for the Fe active centers taking place in the first stages of the peroxide addition. Since it is well known that NOM has an important ability to complex metal ions [36], it is very plausible that aromatic NOM molecules established a coordinative interaction with the metal sites embedded into the catalyst pores in such early stages of CWPO reaction. Thereafter, once the peroxide molecules achieved a minimum critical interaction with the active metal, the NOM depletion by hydroxyl radicals began. The optimization of the catalyst/peroxide ratio may clearly allow a further improvement of the catalytic performance exhibited by this Al/Fe-pillared clay, in order to achieve complete COD removal from surface waters at still smaller times of reaction.

The color removal recorded along the same catalytic experiments is shown in Fig. 3. Unlike than for the COD removal, the color depletion in presence of the iron clay catalysts occurred fairly more efficiently than when either only catalyst (catalyst blank), only peroxide (peroxide blank) or only the Al-pillared clay reference



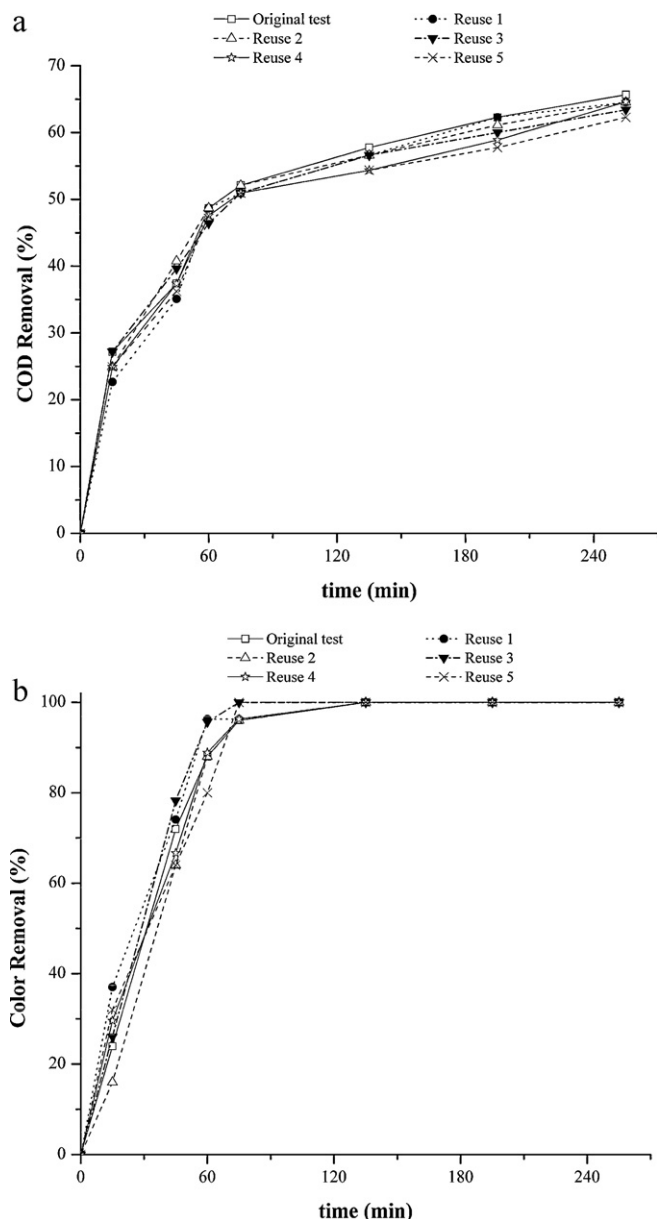
**Fig. 3.** Color<sub>455</sub> removals from raw surface water displayed by the clay catalysts. Set up:  $[\text{color}_{455}]_0 = 42 \text{ PCU}$ ; catalyst loading =  $0.5 \text{ g/dm}^3$  for all solids excepting sample BVAIFe2C-EtOH25- $5.0 \text{ g/dm}^3$ ;  $[\text{H}_2\text{O}_2]_{\text{added}} = 0.047 \text{ mol/dm}^3$ ;  $\text{H}_2\text{O}_2$  addition flow rate =  $6.0 \text{ cm}^3/\text{h}$ ; final stoichiometric ratio  $[\text{H}_2\text{O}_2]/[\text{COD}]_0 = 1.0$ ; pH of reaction = 3.7; temperature =  $291 \pm 2.0 \text{ K}$ ; pressure = 72 kPa.

(BVAI-W2) were present. Among them, peroxide alone showed to be particularly poor for color elimination. All the Fe-modified materials attained 100% of color depletion below 75 min of treatment (60 min of CWPO reaction). Moreover, catalyst BVAIFe2C-EtOH25 at  $5.0 \text{ g/dm}^3$  was able to perform the same within 60 min of treatment (45 min of reaction). It demonstrates that CWPO reaction is very efficient in the NOM removal from natural waters, especially when their content represents significant color problems in resulting drinking water. It probably can be explained because of the extremely high reactivity towards aromatic compounds displayed by the hydroxyl radical [37], being such a hydrophobic fraction (humic and fulvic species) at the same time one of the main responsible for providing organic color to raw surface waters like the used in the present study [4]. Moreover, the profile of color removal observed for all the Fe-modified materials was almost undistinguishable confirming as before that neither, clay concentration, suspension medium or metal concentration employed in the intercalating step affected significantly the color depletion from the raw surface water. The catalyst BVAIFe2C-EtOH25 used under the higher loading ( $5.0 \text{ g/dm}^3$ ) was able to anticipate at least 15 min the full color removal.

The strong overlapping between the catalytic performances displayed by all of the modified materials in color removal contrasts with the clearly different profiles of COD removal exhibited by the same catalysts. It is probably due, as mentioned above, to a faster attack of active radicals on the hydrophobic fraction responsible of color. It shows, at the same time, that color removal does not unambiguously imply total mineralization of such a fraction but only highly specific rupture of the chromophore centers therein involved along the earlier stages of reaction.

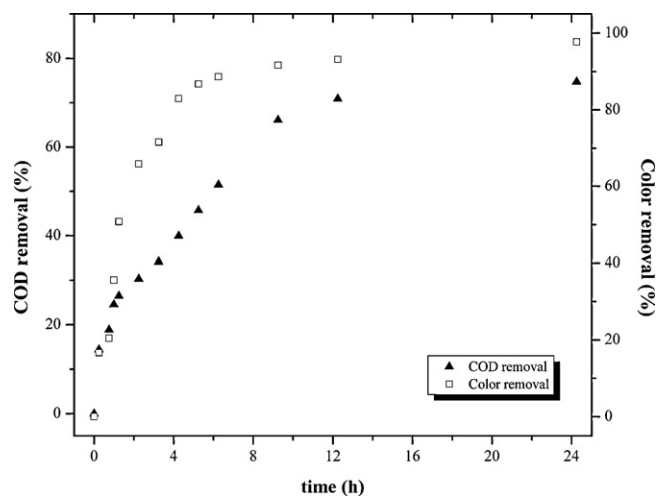
### 3.3. Catalyst reuse and stability

AAS analyses of the output streams showed concentrations of dissolved iron always below  $0.5 \text{ mg/dm}^3$ , indicating that very low contributions of observed COD or color removals could be



**Fig. 4.** (a) COD removals displayed by reuse of BVAIFe<sub>2</sub>C-EtOH<sub>25</sub> catalyst. Set up:  $[\text{COD}]_0 = 40.14 \text{ mg O}_2/\text{dm}^3$ ; catalyst loading =  $0.5 \text{ g}/\text{dm}^3$ ;  $[\text{H}_2\text{O}_2]_{\text{added}} = 0.047 \text{ mol}/\text{dm}^3$ ;  $\text{H}_2\text{O}_2$  addition flow rate =  $6.0 \text{ cm}^3/\text{h}$ ; final stoichiometric ratio  $[\text{H}_2\text{O}_2]/[\text{COD}]_0 = 1.0$ ; pH of reaction = 3.7; temperature =  $291 \pm 2.0 \text{ K}$ ; pressure = 72 kPa. (b) Color<sub>455</sub> removals displayed by reuse of BVAIFe<sub>2</sub>C-EtOH<sub>25</sub> catalyst. Set up:  $[\text{color}_{455}]_0 = 42 \text{ PCU}$ ; catalyst loading =  $0.5 \text{ g}/\text{dm}^3$ ;  $[\text{H}_2\text{O}_2]_{\text{added}} = 0.047 \text{ mol}/\text{dm}^3$ ;  $\text{H}_2\text{O}_2$  addition flow rate =  $6.0 \text{ cm}^3/\text{h}$ ; final stoichiometric ratio  $[\text{H}_2\text{O}_2]/[\text{COD}]_0 = 1.0$ ; pH of reaction = 3.7; temperature =  $291 \pm 2.0 \text{ K}$ ; pressure = 72 kPa.

attributed to homogeneous metal activation of peroxide. Besides, catalyst BVAIFe<sub>2</sub>C-EtOH<sub>25</sub> was reused along six consecutive semi-batch experiments, without significant loss of activity as can be seen in Fig. 4(a and b) (COD removal at final time of reaction declined from 65.7% to 62.3%; true color<sub>455</sub> removal at 60 min declined from 89% to 80%). The high chemical stability against the metal leaching has been previously verified for such a kind of Fe-modified clay materials for AMR values below 5.0%, thanks to decreased incidence of external oxide aggregates [12]. Then, probably the slight loss in catalytic performance may arise to cumulative, probably irreversible adsorption of high molecular mass organic moieties present in the aqueous influent.



**Fig. 5.** COD and Color<sub>455</sub> removals from humic-doped water by catalyst BVAIFe<sub>2</sub>C-EtOH<sub>25</sub> along prolonged productivity assay. Set up:  $[\text{COD}]_0 = 1185 \text{ mg O}_2/\text{dm}^3$ ;  $[\text{color}_{455}]_0 = 1100 \text{ PCU}$ ; Catalyst loading =  $5.0 \text{ g}/\text{dm}^3$ ;  $[\text{H}_2\text{O}_2]_{\text{added}} = 0.67 \text{ mol}/\text{dm}^3$ ;  $\text{H}_2\text{O}_2$  addition flow rate =  $2.0 \text{ cm}^3/\text{h}$ ; final stoichiometric ratio  $[\text{H}_2\text{O}_2]/[\text{COD}]_0 = 1.0$ ; pH of reaction = 7.5; temperature =  $291 \pm 2.0 \text{ K}$ ; pressure = 72 kPa.

In the other hand, Navalon et al. [38] have recently proposed that reusability in several runs is not a good criterion for stability since it depends on the substrate-to-catalyst ratio, and then a prolonged experiment under a very high ratio should be preferable to rank the true catalyst stability. Besides, the requirement of pH control has been claimed to be a serious drawback of either, homogeneous or heterogeneous Fenton catalysts, preventing their extended implementation in the treatment of real contaminant streams at big scale [4,38,39]. Thus, in order to estimate the maximal productivity of catalyst BVAIFe<sub>2</sub>C-EtOH<sub>25</sub> in the application here proposed, an extra assay was performed under a very high demanding substrate-to-catalyst ratio, throughout 24 h of reaction (Fig. 5). As can be seen, the use of almost thirty-fold times higher ratio between the substrate and the catalyst with respect to the precedent runs (Figs. 2 and 3) led to a decrease in the final COD removal from 96% to around 75%, for identical peroxide stoichiometric dosage, while the color removal at 6 h of reaction (the time spent for feeding 25% of the peroxide dose, in turn the amount required for full color removal in the former run) was close to 90%. Moreover, such a decrease in the catalytic performance results seemingly low compared with the same solid under a catalyst loading of  $0.5 \text{ g}/\text{dm}^3$  (ten times lower) performing on the raw surface water, where maximal COD removal at total peroxide dosage was around 65%. Then, the catalyst still carried out a better use of the oxidizing agent even under the extremely high concentration of humic substances employed as substrates. This can be due to the slower rate of peroxide addition, giving increased chances for the catalyst to accomplish the activation to radicals, reducing the incidence of side reactions. However, in terms of color removal, the productivity resulted more affected under high substrate-to-catalyst ratio. As can be seen in run BVAIFe<sub>2</sub>C-EtOH<sub>25</sub>- $0.5 \text{ g}/\text{dm}^3$  at Fig. 3, total color depletion is achieved at 75 min under normal conditions, that is, 1 h of oxidizing reaction, whereas the same catalyst only removed close to 98% of the initial color at total peroxide dosage (24 h) in the prolonged test. It may arise to decreased adsorption of humic substances by the clay catalyst at the close to neutral pH or reaction employed in the maximal productivity test. Since most of the carboxylate groups pending from aromatic structures featuring this kind of substances must be present in anionic form under neutral pH [40], the adsorption on the still negatively charged platelets of the clay may become strongly inhibited. Thus,



the color removal under such conditions of pH must be addressed mainly by oxidation, without significant contribution of adsorption on the catalyst surface. This may also partially explain the higher relative efficiency displayed by the same catalyst in the COD removal with respect to the case of diluted substrate, because decreased organic adsorption may allow increased interaction of the peroxide molecules with the catalyst surface through the earlier stages of reaction. Finally, it is remarkable the low sensibility of the clay catalyst to perform in the reaction as a function of the pH of reaction. As said, an optimal pH of operation for both homogeneous and heterogeneous Fenton processes based in iron species has been established, never exceeding 4.0 [27]. Moreover, and in spite of the increased incidence of peroxide self-decomposition reaction expectable at increased pH of work [41], the catalyst BVAFe<sub>2</sub>C-EtOH<sub>25</sub> displayed a pretty high catalytic performance under close to neutral pH and very high substrate strength.

#### 4. Conclusions

A series of Al/Fe-pillared clays prepared from concentrated precursors have been tested as active solids in the catalytic wet peroxide oxidation of NOM present in raw surface water. The metal speciation by Ferron analyses as a function of total concentration and hydrolysis ratio, allowed the determination of an improved hydrolysis ratio of 1.6 for the preparation of the concentrated mixed pillaring precursor having a final [Al+Fe] close to 0.63 mol/dm<sup>3</sup>. The preparation of the clay catalysts from such a concentrated mixed Al/Fe oligomeric precursor and a concentrated ethanol-based suspension resulted advantageous not only in terms of lower volume of suspension to be handled (more than ten times lower), but also by the improved catalytic performance displayed by the final materials, against the diluted and water-based precursors. High concentration in the metal precursor led to slightly decreased and broadly distributed basal spacings measured by XRD, but also higher compensation of the cationic exchange capacity of the starting clay. Partial transformation of Al<sub>13</sub> Keggin-like polycations to highly charged Al<sub>30</sub> units under high metal concentration and prolonged thermal treatment is hypothesized to explain it. The use of ethanol as suspension medium, exhibiting significantly lower dielectric constant than water, led to a pattern of expansion of the clay mineral fairly less susceptible to the concentration of the clay suspension.

The clay catalysts exhibited high NOM removal for raw surface water, being depleted over 95% of the COD in 4 h and 100% of the true color<sub>455</sub> in less than 45 min of reaction for a conventional substrate-to-catalyst ratio. The catalysts also showed remarkable high stability against chemical leaching of the active metal from hosting aluminosilicate along several catalytic tests. Furthermore, a high demanding productivity test was carried out under a very high substrate-to-catalyst ratio, pH 7.5 and prolonged time of operation (24 h), by employing humic substances extracted from a lignite-type mineral to simulate NOM charge. The material prepared from the concentrated metal precursor and the 25%, w/v clay suspension in ethanol successfully overpassed the test, showing decreased COD removal at total time of reaction but still more efficient use of the peroxide solution, even considering the less optimal for Fenton, close to neutral pH of reaction used. CWPO developed with Al/Fe-pillared clays prepared from concentrated precursors is claimed as an excellent heterogeneously catalyzed Fenton-like technology useful for NOM removal in drinking water production processes.

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